

PHOTOCHEMICAL MODIFICATION OF DIAMOND FILMS: A STRUCTURAL AND MECHANISTIC STUDY

Beth M Nichols, Robert J Hamers

Department of Chemistry, University of Wisconsin-Madison, Madison ,WI

James E. Butler, John N Russell, Jr.,

Chemistry Division, Naval Research Laboratory, Washington D.C.

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Abstract

Diamond and diamond films have many properties which make them attractive substrates for developing technologies in fields such as biotechnology, biological and chemical sensing, and molecular electronics. Previous work has shown that hydrogen-terminated nanocrystalline diamond films can be covalently modified with molecules bearing a terminal vinyl ($C=C$) group by way of a photochemical process under 254 nm light.[1] While this method has been shown to produce stable monolayer films, the reaction mechanism and film structure have not been previously investigated. The mechanism is particularly intriguing because it proceeds using sub-bandgap excitation energy. Here, we report an investigation of the structure and mechanism of the photochemical modification of diamond with functionalized terminal alkenes.

X-ray photoelectron spectroscopy experiments were performed on nanocrystalline diamond films and on single-crystal diamond samples. A comparison of the rates of photochemical modification of single crystal diamond (111) and nanocrystalline diamond films shows no significant difference in reactivity, demonstrating that the modification process is not controlled by grain-boundaries or other defects associated with the polycrystalline films. By using a molecule with a fluorine “tag” at one end, we can establish the degree to which the molecules are oriented on the surface using angle-resolved XPS measurements. These measurements show that the fluorine tag is at the exposed (vacuum) interface, thereby ruling out the possibility of polymerization onto the surface and establishing that the molecules bind to the surface via the olefin group.

To understand the mechanism of photochemical modification, we have conducted a number of experiments aimed at identifying how photoexcitation of the bulk diamond induces the surface chemical modification. Previous work has shown that hydrogen-terminated single crystal diamond exhibits negative electron affinity,[2-4] and we find that our nanocrystalline diamond samples also exhibit negative electron affinity. These results suggest that direct photoejection of electrons into the organic fluid may be responsible for the photochemical modification. Previous studies have shown that 254 nm light is sufficient to eject electrons from diamond surfaces into vacuum.[5] Since electrons are stabilized by a polarizable medium, it should also be possible to directly eject electrons from diamond into an organic liquid film. Such photoejection would alter the diamond electronic structure and would produce ions in the organic liquid. Since ions are often highly reactive, we propose that direct photoejection of electrons from diamond into the liquid induces the overall photochemical reaction. Using gas chromatography-mass spectrometry (GC-MS), we have analyzed the changes in chemical composition of 1-dodecene and trifluoroacetamide-protected 10-aminodec-1-ene after illumination with 254 nm light in contact with diamond. Our results show the formation of new chemical products in solution that are only formed when the diamond film is present, indicating that optical absorption within the diamond is necessary for the changes in solution chemical composition. The identity of these species and their use in the interpretation of the reaction mechanism will be discussed.

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